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"The Distribution of n-Alkanes in Partially Frozen Middle Distillate Fuels"

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INTRODUCTION

This work on partially frozen fuels is one of a continuing series of studies on the effect of composition on the freezing properties of hydrocarbon fuels (1-6). The method used for this purpose was reported previously (4-7). By means of this method we were able to determine the composition of the liquid and solid phases in partially frozen mixtures consisting of liquid and of solid crystals plus entrapped liquid. This paper presents the results of this study on five different middle distillate fuels.

FUEL SAMPLES

Five fuel samples were used in this study: three Navy jet fuels (JP-5) and two Navy ship propulsion diesel fuels (DFM). The three jet fuels included a shale-derived fuel (NRL No. J-22) from the Shale-II refining process conducted by the Standard Oil Company of Ohio (SOHIO) at their refinery at Toledo, Ohio (8-10). The other two were conventional petroleum-derived JP-5 fuels (NRL Nos. 80-5 and 81-19). Fuel 81-19 contained very low concentrations of n-alkanes compared to those in the other two fuels. All three met the military specification requirements for JP-5 jet turbine fuel (11). The freezing points (12) of J-22, 80-5, and 81-19 fuels, -48° , -49° , and -53°C ., respectively, were below the specification requirement of -46°C maximum (11).

One of the samples of diesel fuel studied [82-8] was a conventional petroleum-derived DFM. The other [82-16] was a shale-derived fuel also from SOHIO's Shale-II refining process. The pour points (13) of the two DFM fuels, -11° and -23°C respectively, were well below the military specification requirement of -6.7°C maximum (11).

FUEL ANALYSES

Quantitative analyses of the n-alkane compositions in the fuels were made using a 50-m (OV-101), fused silica 0.2-mm i.d. capillary column in a Hewlett-Packard 5880 gas chromatograph (GC) or when necessary by combined GC/MS (EI mode). The n-alkane concentrations in all five original fuel samples are listed in Table 1.

PARTIALLY FROZEN FUELS

The residual liquid ("filtrate") from partially frozen fuel samples was separated from the "precipitate" (crystalline material plus entrapped liquid) and collected by means of the NRL liquid-solid separator apparatus (LSS) at several temperatures below the freezing points of the original fuel samples. The LSS method was described previously (6,7). The filtrate and precipitate were characterized by gas chromatography. The GC chromatograms for all five fuels and their associated filtrates and precipitates are all quite similar, although there are significant differences which affected the ease and accuracy of the quantitative analysis.

TABLE 1
n-Alkane Concentrations in Original Fuel Samples
($X_0 = \% w_0/w_0$)

n-Alkane	JP-5			DFM	
	Shale II	Petroleum	Petroleum	Shale II	Petroleum
	NRL No.	J-22	80-5	81-19	82-16
C ₈				0.07	0.07
C ₉				0.17	0.12
C ₁₀	4.50	1.01	0.21	0.53	0.40
C ₁₁	8.55	4.36	0.82	1.11	0.60
C ₁₂	7.10	5.35	1.01	1.61	1.00
C ₁₃	4.41	3.78	1.30	2.54	1.44
C ₁₄	1.36	1.67	0.82	2.91	1.88
C ₁₅	0.35	0.54	0.45	2.66	2.00
C ₁₆		0.15	0.16	2.30	1.89
C ₁₇			0.06	2.26	1.63
C ₁₈				1.60	1.22
C ₁₉				0.68	1.08
C ₂₀				0.06	0.71
C ₂₁					0.50
C ₂₂					0.30
C ₂₃					0.16
C ₂₄					0.07
Total %	26.27	16.86	4.83	18.50	15.07

RESULTS AND DISCUSSION

Filtrate

The filtrate solubility data for the five fuels are plotted as the logarithm of n-alkane concentration in the filtrate (as weight percent) vs the reciprocal absolute temperature (1000/T K). Three of these plots are shown in Figures 1-3. For each of the five fuels, the data for all the n-alkanes form straight lines, as would be expected for a Van't Hoff solubility plot. All of the slopes were determined by a least squares fit of the data.

The six n-alkanes present in measurable quantities in the J-22 jet fuel are plotted in Fig. 1. The slope of the line for the lowest n-alkane, n-C₁₀, is very slightly positive, and the next n-alkane, n-C₁₁, the line is almost horizontal. The data for the remaining n-alkanes show definite negative slopes which increase in magnitude with carbon number. The shaded points in Fig. 1 represent the original fuel concentrations for each alkane plotted at the freezing point (-48°C). Since this temperature (actually the melting point) is the point at which the last trace of solid material redissolves, the composition at this point should be the same as that of the liquid fuel. As expected, these concentrations fell close to the plotted lines in almost all cases.

The n-alkanes present in the petroleum-derived jet fuel 80-5 were n-C₁₀ - n-C₁₆. The slopes of the curves for the two smallest n-alkanes, n-C₁₀ and n-C₁₁, were perfectly flat. The data for fuels 80-5 and J-22 indicate that the normal alkanes behave in an identical manner when the fuels are partially frozen.

For the low-n-alkane jet fuel, 81-19, the data are plotted in Fig. 2 for the five highest n-alkanes. The lines for C₁₀ and C₁₁ (omitted for clarity) are perfectly flat, and the line for C₁₂ is almost so. The three highest n-alkanes, C₁₄

through C₁₆, show definite slopes which increase in magnitude with the carbon number, thus showing close agreement with the higher n-alkanes in the other fuels studied.

The data for C₁₃ in the 81-19 fuel, however, follow a different pattern, as is clearly evident. Not only are the data widely scattered from the straight line obtained by linear regression from the six data points, but the line itself shows a slight increase in concentration with decreasing temperature. Also, unlike the other n-alkanes, the extrapolated concentration at the freezing point is considerably lower than its concentration in the original fuel. This suggests that n-C₁₃ may have an opposite effect on the freezing point of fuels to that of the other n-alkanes. This anomalous effect of n-C₁₃ has been reported elsewhere (1,3,5), where the effect of n-C₁₃, in certain cases, was to lower the freezing point rather than to raise it.

The two diesel fuels show a much wider spectrum of n-alkanes, from n-C₈ to n-C₂₀ in the shale-derived 82-16, and from n-C₈ to n-C₂₄ in the petroleum-derived 82-8. The filtrate data for fuel 82-8 are plotted in Figure 3. For the sake of clarity the data for the lower alkanes were not plotted in Figure 3. The behavior of the n-alkanes in fuel 82-8, are very similar to that in the other fuels.

A careful study of the fuel and filtrate chromatograms failed to reveal any other components in any of the five fuels whose concentration in the filtrate was regularly lower than that in the fuel. Therefore a conclusion, indicated by a study of the filtrate data above, is that only the n-alkanes freeze or crystallize out of the fuel in the temperature ranges studied, which in each case was in the vicinity of the freezing point of that fuel. The filtrate data demonstrate the importance of the role of the higher n-alkanes in the freezing of jet and diesel fuels.

Precipitate

The precipitates for all five fuels consisted of a waxy crystal matrix and varying, significant amounts of entrapped liquid (filtrate). In the previous paper we have shown how the concentrations of the n-alkanes in the crystalline solids can be obtained from the filtrate and precipitate concentrations (7). The key to determining the concentrations in the solid phase was seen to lie in the value of "Z", (the liquid fraction of the precipitate), and this in turn depended upon the suitable choice of non-crystal-forming reference components.

Choice of *K* Components for Estimating Z

Two components (clearly defined in the GC traces and identified by GC-mass spectrometry as 4-methyl-decane and 2-methyl-dodecane) were chosen as *K*-components for the jet fuel J-22. Very satisfactory results were obtained by using them to determine the values of Z.

A study was made of the GC traces of each of the other fuels, from which a number of components were chosen as *K*-components. For each fuel, average Z-values were thus estimated. The details of the selection of *K*-components was described previously (6).

Variation of Solid Fraction with Temperature

Once the value of Z was determined, it was a simple matter to find the solid fraction in the precipitate, and then the percent solids in the partially frozen fuel sample (6,7). The percent of crystalline solids, S, as a function of temperature is shown for all five fuels in Fig. 4.

The lines in Fig. 4 may be extrapolated to zero (S = 0) with resulting temperatures corresponding to the freezing point (more correctly, the "melting

point"). This is because in the determination of the freezing point of fuels, the freezing point is defined as the temperature at which the crystals formed on cooling just disappear when the temperature is allowed to rise (12). The extrapolated temperatures are shown in Table 2. The experimentally determined freezing points for the JP-5 fuels (Table 2) are in agreement with the extrapolated values within experimental error. Furthermore, the extrapolated temperature of -46°C for the Shale-II JP-5 fuel (J-22) is in good agreement with the extrapolated data obtained by Moynihan et al (14) who investigated the same fuel in their studies of partially frozen fuels using a dye tracer technique for the separations.

TABLE 2
Extrapolated vs. Experimental Freezing Point Data

Fuel	Experimental (°C)	Extrapolated (°C)	
	Freezing Point (12)	S = 0	X _G " = 0*
JP-5 (J-22)	-48	-46	-48
" (80-5)	-49	-48	-48
" (81-19)	-53	-56	-54
DFM (82-16)	-23**	-14	-16
" (82-8)	-11**	- 4	- 4

* Averaged data

** Pour Point (13)

There are no freezing point requirements for DFM and therefore no corresponding data for the above DFM fuels. The pour points were determined (13), and are shown in Table 2. Since the pour point of a fuel is a function of flow properties (viscosity and amount of crystallization which has taken place) an increased quantity of solid material (relative to that at the freezing point) is involved. Since this requires further chilling (below the freezing point) it would be expected that pour points should be lower than freezing points. In this case the pour points are 9° and 7° below the extrapolated "freezing point" temperatures for the DFM fuels 82-16 and 82-8 respectively.

Total Material Balance

Table 3 lists the total material balances together with the values obtained for Z, the liquid fraction in the precipitate, and S, the weight percent of crystals

TABLE 3
Total Material Balances

Fuel	JP-5			DFM	
	Shale II	Petroleum	Petroleum	Shale II	Petroleum
NRL No.	J-22	80-5	81-19	82-16	82-8
Temp.(°C)	-53.6	-56.3	-64.4	-28.1	-11.1
% Filtrate (F)	79.6	73.2	69.4	79.8	87.0
% Precipitate (P)	19.9	26.3	29.6	19.6	11.7
% Recovery	99.5	94.5	99.0	99.4	98.6
% Solids (S)	4.5	5.3	1.7	5.5	2.6
Z*	0.77	0.80	0.94	0.72	0.78

*Fraction liquid (filtrate) in precipitate (P)

formed, from a typical run for each fuel. Data for all the experimental runs have been given elsewhere (5,6), but the data presented in Table 2, at roughly the middle of the temperature range investigated, give a good comparison of the values of Z obtained for each fuel.

n-Alkane Concentration in the Solids

The concentration of each n-alkane in the solid phase was calculated by the previously described method (6,7).

All five fuels show the same characteristic behavior: the higher the n-alkane the greater its concentration increase in the solid phase. The concentrations of the lighter n-alkanes generally show an increase in concentration in the solids as the temperature decreases, which is to be expected as more crystals freeze out of the liquid phase and form part of the solid phase. The heavier n-alkanes, on the other hand, form most of the solid phase at the higher temperatures, and will form a proportionately lower fraction as more of the other n-alkanes freeze out as the temperature decreases.

Percent of the n-Alkanes in the Fuel Found in the Solid Phase

Of great significance is the percent (or fraction) of each n-alkane present in the original fuel that appears in the solid phase, X_S'' . This tells us the distribution of the n-alkanes in partially frozen fuels. X_S'' depends on the concentration of the n-alkane in the original fuel, in the filtrate and in the precipitate, as well as on the value of Z (7).

Figs. 5-7 show the values of X_S'' plotted as a function of the temperature for three of the five fuels. In most cases the graphs are linear. In almost every case the rate of increase in the percent of n-alkane appearing in the solid phase increases with the carbon number.

For the fuel J-22, the data plotted in Fig. 5 show a slight but steady increase in the percent of n-C₁₀, the lowest n-alkane present that appears in the solid phase, reaching a value of about 4% at -58°C. The higher n-alkanes show increasing amounts appearing in the solid phase with over 75% of n-C₁₅ in the solids at -58°C. It may be, however, that there is no longer a straight-line relationship near this lower temperature for the two highest n-alkanes. Obviously the percent in the solids must approach 100% more slowly the closer it gets to 100%. If all the lines for the six n-alkanes are extrapolated to $X_S'' = 0$ (the freezing point temperature is found to be an average value of -47.9°C. Similar extrapolated data for all five fuels ($X_S'' = 0$) are shown in Table 2. These extrapolated freezing points ($X_S'' = 0$) compare well with actual freezing points, as well as with extrapolated data from $S = 0$, as can be seen in Table 2.

The normal alkanes are thus seen to behave as would be expected if they alone freeze or crystallize out of the fuel at temperatures below, but in the vicinity of, the freezing point. The higher the n-alkane the more completely it is removed from the liquid phase as the temperature decreases.

Individual n-Alkane Balances

For every run, a material balance for each of the n-alkanes and A-components present was carried out. With very few exceptions the amount of each n-alkane in the total liquid and in the solid was found to be within 5% of that in the original fuel. Where the concentrations were very low, as with n-C₂₃ and n-C₂₄ in fuel 82-8, the deviation approached 20%.

Composition of the Solid Phase

Probably the most important and certainly the most difficult task we had was the determination of the composition of the solid phase. The actual concentrations of the n-alkanes are not reported here, but they are obtainable from the earlier NRL studies (5,6).

In the case of the J-22 fuel, at two temperatures, -58° and -54°C , the n-alkanes account for over 95% of the solids formed. About 1% seems to be due to the k-compounds. There are undoubtedly some other compounds in the 67% of the J-22 fuel (that is not made up of n-alkanes or of the k-compounds) that form crystals in the solids. Nevertheless no compounds other than the n-alkanes could be found having higher concentrations in the precipitate than in the filtrate, and so no compounds other than n-alkanes form crystals to any great extent. The other fuels followed the same pattern, but the percentage of n-alkanes in the solid phase was not as high as that of the J-22 fuel.

Until other methods of analysis can be devised to measure accurately small amounts of many different components, or until the solid crystals can be separated completely from the entrapped liquid and then analyzed, the complete composition of the solid crystalline phase will remain undetermined. Further useful information, however, might be gathered, by partially freezing some mixtures of normal alkanes with one or two other components and determining their distribution coefficients. Extrapolation from this to their behavior in fuels might be made and tested.

SUMMARY AND CONCLUSIONS

The liquid (filtrate) and the solid crystals containing a large portion of entrapped liquid (precipitate) from partially frozen samples of five middle distillate fuels were separated from each other and collected by means of the NRL liquid-solid separator (LSS). The fuels consisted of three different types of JP-5 jet fuel and two different types of DFM Navy ship propulsion fuel. The separations were made at several temperatures, each below the freezing point of the original fuel samples. The original samples and the collected precipitate and filtrates were analyzed quantitatively by GC (or when necessary by combined GC/MS). The filtrate data for all five fuels were straightforward, and Van't Hoff plots of the n-alkane concentrations (log concentrations vs reciprocal absolute temperature) formed straight lines and their slopes demonstrated the importance of the higher n-alkanes in fuel freezing, or crystallization, at cold temperatures. The precipitates, which consisted of a waxy crystal matrix, all entrapped significant amounts of liquid (filtrate). An indirect method (using k-compounds), which was described in an earlier paper, was used to estimate the n-alkane concentrations in the solid fraction of the precipitate.

The solids data demonstrated that the higher n-alkanes play the key role in fuel crystallization at low temperatures, concentrating as much as tenfold in the crystallized solids compared to the liquid. Also it was shown that the n-alkanes form the major part, up to at least 95% by weight in some fuels, of the solid crystals formed.

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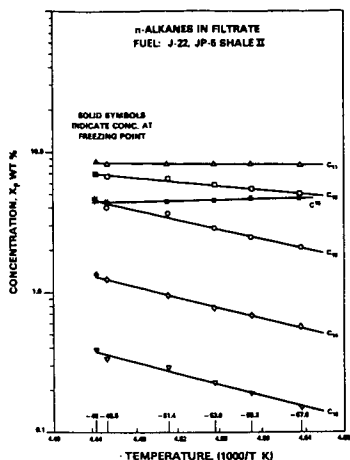


FIGURE 1

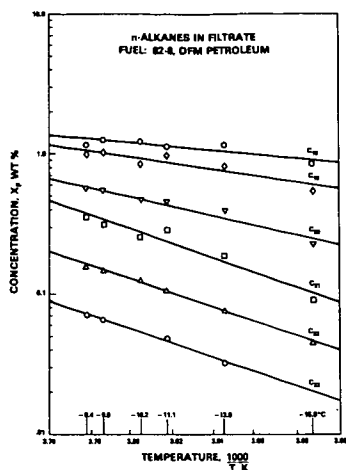


FIGURE 3

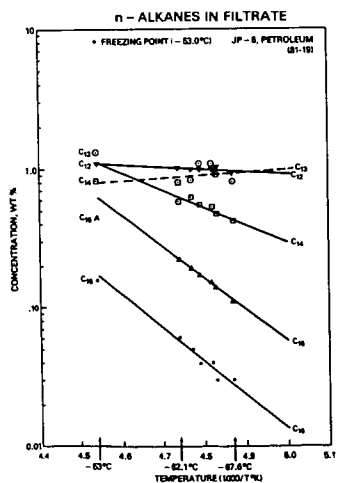


FIGURE 2

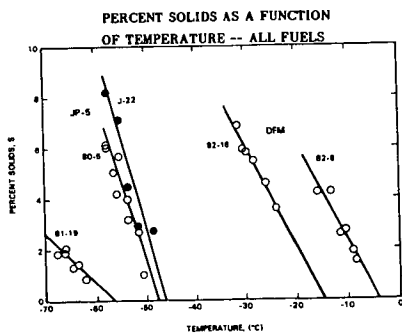


FIGURE 4

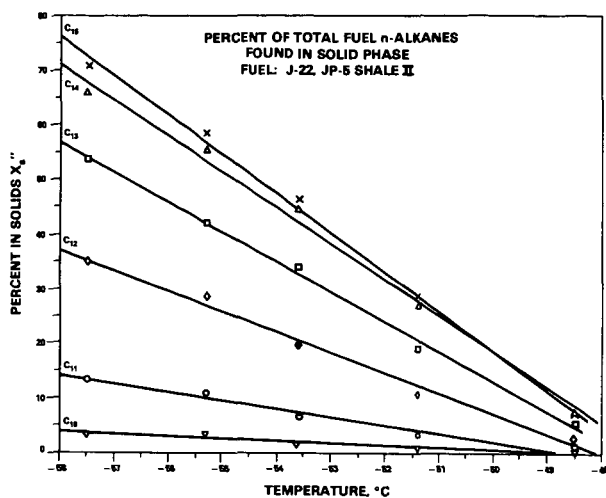


FIGURE 5

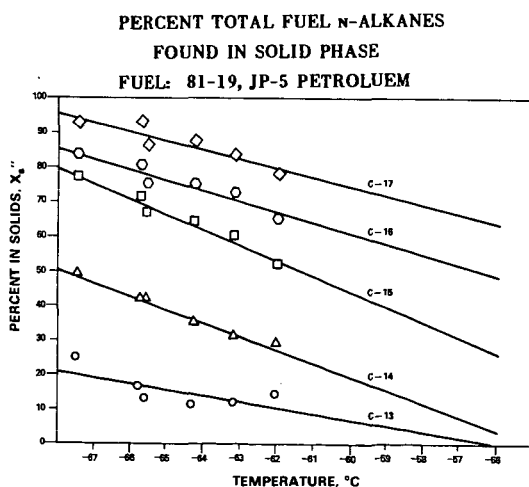
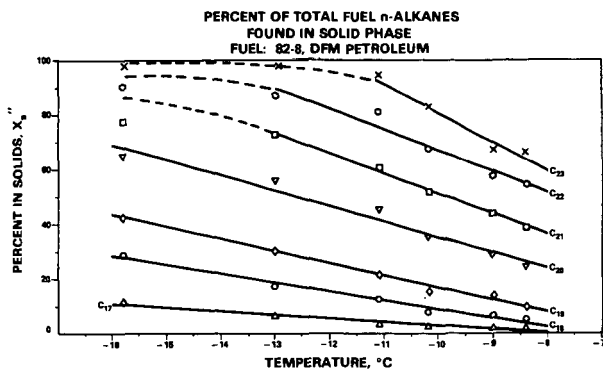


FIGURE 6



NOMENCLATURE

	Fuel Sample	Filtrate	Precipitate	Precipitate Fraction Solid	Precipitate Fraction Liquid
<u>Total Material:</u>					
Weight	W_s	W_f	W_p	W_s	W_L
Fraction of Sample		$F = W_f/W_s$	$P = W_p/W_s$	$S = W_s/W_s$	$L = W_L/W_s$
<u>SPECIES a or k:</u>					
Weight	w_a	w_f	w_p	w_s	w_L
Concentration (w/W)	$X_a = w_a/W_s$	$X_f = w_f/W_f$	$X_p = w_p/W_p$	$X_s = w_s/W_s$	$X_L = w_L/W_L$
$Z = W_L/W_f$					
a = Crystalline Species					
k = Noncrystalline Species					
<u>Subscript:</u>				<u>Superscript:</u>	
o = Original Sample				* = Normalized Data (Concentration divided by that of original sample)	
F = Filtrate					
P = Precipitate				$^{\circ}$ = Percent concentration of a species in the fuel found in the solid phase	
S = Solids Fraction of Precipitate (Crystals)					
L = Liquid Fraction of Precipitate					
T = Total					